Atomic Energy Control Board
P O Box 1046
Ottawa, Canada
K1P 5S9

Commission de contrôle de l'énergie atomique
C P 1046
Ottawa, Canada
K1P 5S9

INFO-0211

DEVELOPMENT OF AN AUTOMATED METHOD FOR DETERMINATION OF THORIUM IN SOIL SAMPLES AND AEROSOLS

by

J.E. Stuart and R. Robertson
Becquerel Laboratories Inc.

A research report prepared for the
Atomic Energy Control Board
Ottawa, Canada

September 1986

Canada

Research report

DEVELOPMENT OF AN AUTOMATED METHOD FOR DETERMINATION OF THORIUM IN SOIL SAMPLES AND AEROSOLS

Experimental work carried out by J.E. Stuart and R. Robertson and report prepared by J.E. Stuart under contract to the Atomic Energy Control Board

ABSTRACT

Methodology for determining trace thorium levels in a variety of sample types was further developed.

Thorium in filtered water samples is concentrated by ferric hydroxide precipitation followed by dissolution and co-precipitation with lanthanum fluoride. Aerosols on glass fibre, cellulose ester, or teflon filters and solid soil and sediment samples are acid digested. Subsequently thorium is concentrated by lanthanum fluoride co-precipitation. Chemical separation and measurement is then done on a Technicon AA11-C autoanalyzer, using solvent extraction into thenoyltrifluoroacetone in kerosene followed by back extraction into 2 N HNO_3, and colourometric measurement of the thorium arsenazo III complex. Chemical yields are determined by the addition of thorium-234 tracer using gamma-ray spectrometry. The sensitivities of the methods for water, aerosol and solid samples are approximately 1,0 µg/L, 0,5 µg/g and 1,0 µg/g respectively. At thorium levels about ten times the detection limit, accuracy is estimated to be ± 10% for liquids and aerosols and ± 15% for solid samples, and precision ± 5% for all samples.

RÉSUMÉ

Le présent rapport rend compte d'une méthode qui a été perfectionnée pour déterminer le niveau de thorium à l'état de traces dans divers types d'échantillons.

Le thorium contenu dans les échantillonnages d'eau filtrée est concentré par la précipitation d'hydroxyde ferrique, suivie de dissolution et de co-précipitation avec du fluorure de lanthanum. Les aérosols présents sur la fibre de verre, l'ester de cellulose ou les filtres de téflon, ainsi que les échantillons de sol et de sédiments solides sont digérés dans un acide. Par la suite, le thorium est concentré par co-précipitation avec du fluorure de lanthanum. La séparation chimique et le relevé sont ensuite effectués par auto-analyseur «Technicon AA11-C» qui extrait d'abord le lanthanum par dissolution du thorium dans du thénoyltrifluoroacétone (TTA) mêlé à du kérosène, puis qui extrait le TTA et le kérosène par dissolution du thorium dans du 2 N HNO_3, et qui fait enfin un relevé colorimétrique du complexe arsenazo III du thorium. Le rendement chimique est déterminé par l'addition de traceurs de thorium 234 et l'utilisation de méthodes de spectrographie gammagraphique. La sensibilité des méthodes pour les échantillons d'eau, d'aérosols et de solides est d'environ 1,0 µg/L, 0,5 µ/g et 1,0 µg/g, respectivement. À des niveaux de thorium 10 fois supérieurs à la limite de détection, la marge d'erreur est estimée à ± 10 pour 100 pour les échantillons de liquides et d'aérosols, et à ± 15 pour 100 pour les échantillons de solides; la précision est estimée à ± 5 pour 100 pour tous les échantillons.

DISCLAIMER

The Atomic Energy Control Board is not responsible for the accuracy of the statements made or opinions expressed in this publication and neither the Board nor the authors assume liability with respect to any damage or loss incurred as a result of the use made of the information contained in this publication.

PREFACE

The method developed for AECB project No. H1103472220 has been further refined to eliminate the manual ion exchange step in the solid sample preparation and provide a single methodology for the Technicon AAII-C Autoanalyzer that is capable of analyzing all sample types.

Laboratory testing has been carried out on tap water, simulated aerosol samples, soil samples, lake and stream sediments, and a rock sample known to have a high thorium level (65 ppm) and high levels of the major interferants zirconium and hafnium.

TABLE OF CONTENTS

ABSTRACT i

PREFACE ii

A. SAMPLE PREPARATION..... 1

1. Introduction..... 1
2. Preparation of Water Samples 1
3. Preparation of Solid and Aerosol Samples..... 2
4. Thorium-234 Tracer Preparation 3

B. AUTOANALYZER METHODOLOGY 5

1. Introduction 5
2. Analysis of Water, Aerosol and Solid Samples.. 5

C. SAMPLE THROUGH-PUT..... 6

FIGURE 1..... 8

REFERENCES..... 9

APPENDICES:

APPENDIX A - TABLE 1 - CROSS REACTIVITY
TABLE 2 - RESULTS OF ANALYSIS OF SOLID SAMPLES
TABLE 3 - RESULTS OF ANALYSIS OF AEROSOL SAMPLES
TABLE 4 - RESULTS OF ANALYSIS OF WATER SAMPLES

APPENDIX B - STEPWISE PROCEDURES FOR SAMPLE PREPARATION

APPENDIX C - STEPWISE PROCEDURES FOR TRACER PREPARATION

APPENDIX D - STEPWISE PROCEDURE FOR AUTOANALYZER PROCESS ALL SAMPLES

APPENDIX E - PREPARATION OF REAGENT SOLUTIONS

DEVELOPMENT OF AN AUTOMATED METHOD FOR DETERMINATION OF THORIUM IN SOIL SAMPLES.

A. SAMPLE PREPARATION

1. Introduction

The contract objective was "to develop an automated method, and the corresponding apparatus, for measuring the thorium content of solid (soil and aerosol) samples". In the course of meeting this objective, the analysis for water samples was also reviewed resulting in one single autoanalyzer methodology for all sample types. This required some changes to the water sample preparation so that the final products of the sample preparation steps for each sample type are chemically identical.

Thorium in water samples is concentrated by ferric hydroxide precipitation. The precipitate is then dissolved and thorium co-precipitated with lanthanum fluoride. Aerosol and solid samples are treated virtually identically: the sample is acid digested, and thorium co-precipitated with lanthanum fluoride.

The sample preparation chemistries are based on information and classical procedures in The Radiochemistry of Thorium 1.

2. Preparation of Water Samples

Water samples are collected in polyethylene bottles. Where significant quantities of suspended solids are present, the samples are vacuum filtered over a glass-fibre filter disc as soon as possible after collection. The samples are then acidified to 1% in concentrated nitric acid and stored in polyethylene bottles. Aliquots of 500 ml are transferred to 1000 ml clear plastic beakers (polymethylpentene, PMP) to begin the analysis. Thorium-234 tracer and 5 mg iron (III) (as ferric ammonium sulphate solution) carrier are added.

Ammonium hydroxide solution is added and thorium is concentrated from solution via ferric hydroxide co-precipitaiton.

After allowing at least 1 hour for the hydroxide precipitate to agglomerate and settle, the solution is vacuum filtered through a glass-fibre filter disc under a glass wool plug. The glass wool plug prevents filter blockage and allows rapid filtration. Use of the PMP

beakers for the precipitation allows quantitative transfer of the solution and precipitate to the filter assembly without washing. The collected precipitate is washed on the filter with a few millilitres of water to remove excess alkali. The precipitate is then dissolved and washed through the filter into 50 ml polycarbonate centrifuge tubes, using about 15 ml of 2 N HN03. Centrifugation can be used as an alternative to the filtration step. The clear supernatant of the ferric hydroxide precipitation step is decanted to waste and the precipitate transferred to 50 ml polycarbonate centrifuge tubes where it is centrifuged, water washed and then dissolved about 15 ml 2 N HN03.

Lanthanum carrier solution (5 mg lanthanum) and 3 ml of 14 N hydrofluoric acid are added to co-precipitate the thorium and the precipitate digested for 1 hour in a 80 degree celsius water bath or overnight at room temperature. The tubes are then centrifuged and the supernatant decanted to waste. The precipitate is washed with 10 ml of water, centrifuged and the supernatant decanated to waste.

5 ml of 10% aluminum nitrate (pH 1.5) is added to each tube and mixed with a disposable plastic pateur pipet. The tubes are placed in the 80 degree celsius hot water bath for 15 minutes to effect dissolution of the precipitate.

The pH of the cooled solutions is adjusted to 1.50 $\pm$ .05 with 0.5 N NH40H and/or 0.5 N HN03, and transferred to a 10 ml volumetric flask and made up to 10 ml with 10% aluminum nitrate at pH 1.5.

At this stage, the thorium-234 content of the solution is assayed in the 10 ml volumetric flask by gamma-counting to determine chemical yield which typically will be 85-95%. A 2-3 ml aliquot of the solution is then presented to the autoanalyzer for solvent extraction separation of thorium and colorimetric quantitation against similar solution standards of known thorium concentration.

3. Preparation of Solid and Aerosol Samples

Powdered solid samples (up to 0.5 g, < 100 mesh) are weighed into 100 ml PMP beakers. Aerosol samples typically consist of less than 2 mg aerosol material on 25 mm or 47 mm filter substrates of glass-fibre, cellulose ester or teflon. Each is placed in a 100 ml PMP beaker.

Thorium-234 tracer solution and 5 ml each of half-concentrated nitric, hydrochloric and hydrofluoric acids are added. The beakers are then covered with

plastic watch-glasses and placed on a hot-plate with surface temperature 125 degrees celsius for two hours. During this digestion, filter substrates other than teflon normally dissolve.

The beaker covers are then removed and 25 ml 5% boric acid is added to complex fluoride ion. This solubilises any otherwise insoluble fluorides, especially those of the rare-earths and thorium, which may have formed. Complexation of the fluoride ion may force silica out of solution as a gelatinous precipitate which entrains any insoluble organic materials. About one hour after addition of the boric acid, the beakers are removed from the hot-plate.

The supernatant solution containing the thorium is recovered by vacuum filtration of the solutions through a glass-fibre filter disc. Glass wool plugs are placed over the filters for solid samples to hold back the voluminous precipitate. The precipitate and any aerosol filter residues is washed on the filter with 5 ml of distilled water. The filtrate and washings are collected in a 50 ml polycarbonate centrifuge tube. Lanthanum carrier (5 mg) and 3 ml of concentrated hydrofluoric acid are then added to concentrate thorium from solution via lanthanum fluoride co-precipitation.

A waiting period of about 1 hour on a water-bath at approximately 80 degrees celsius or overnight at room temperature is then allowed for complete precipitation and agglomeration. The tubes are then centrifuged for 5 minutes at 2000 rpm prior to decantation of the supernatant to waste. The precipitate is then washed with 10 ml water and the centrifugation step repeated. The wash solution is decanted to waste and 5 ml of 10% aluminum nitrate solution adjusted to pH 1.5 is added to the precipitate in the tube. Using a disposable polyethylene pasteur pipet, the solution and precipitate are stirred and the tube is then placed on a hot-water bath for about 15 minutes to effect dissolution of the precipitate. The pH of the solution is adjusted to 1.50 $\pm$ .05 using 0.5 N NH_4OH or 0.5 N HNO_3. The solution is then made up to 10 ml in a volumetric flask with the same aluminum nitrate solution and the chemical yield, which will typically be 80-90%, determined by gamma-counting of the thorium-234 tracer.

4. Thorium-234 Tracer Preparation

Thorium-234 (half-life 24.1 days) is generated through alpha-decay of ~ 30 g uranium-238 held as the chloride complex on an anion exchange column. The column bed volume is about 250 ml with dimensions 2.5 x 50 cm. The resin is Bio-Rad AG1-X8 100-200 mesh chloride form conditioned in 9 N HCl.

An amount of uranium (VI) oxide equivalent to ~30 g uranium-238 is dissolved in 1.2 L 9 N hydrochloric acid. The solution is filtered through a glass wool plug to remove any insoluble material and then passed through the column. The uranium is retained on the top 30 cm of the column. Any thorium in the loading solution is washed from the column using 1 L 9 N hydrochloric acid. The column is then ready for use.

The column generates in 1 day sufficient thorium-234 for 12 sample analyses. A generation period of 1 month yields enough tracer for 200 samples. It is recommended that the column be eluted at least once per month whether needed or not in order to avoid excessive concentration of dissolved resin in the free-volume solution, to maintain the column in proper condition and to avoid the build-up of weighable quantities of thorium isotopes. Discard the column after 6 months.

To prepare tracer, thorium isotopes are eluted from the column with 150 ml 9 N hydrochloric acid. This solution is evaporated to about 10 ml and then an equal volume of 9 N hydrochloric acid is added. This solution is passed over a 0.7 x 5 cm bed of the same resin used to make the generator column. This removes traces of uranium. The effluent solution from this second column is then evaporated to dryness. A residue is normally evident which is mainly ion-exchange resin dissolved from the generator column. The residue is dissolved in 10 ml 8 N nitric acid and the solution is passed over a 0.7 x 5 cm bed of the same resin conditioned in 8 N nitric acid. The column adsorbs thorium as a nitrate complex whereas impurities such as dissolved resin and traces of other elements pass through. The column is then washed with 2 x 5 ml 8 N nitric acid. The thorium-234 tracer is eluted with 20 ml 1 N hydrochloric acid and diluted as required.

B. AUTOANALYZER METHODOLOGY

1. Introduction

The autoanalyzer procedure described in this report is based largely on the manual procedure previously used at the AECB Ottawa laboratory: The Colorimetric Determination of Total Thorium. In this contract, the water and aerosol methodology described in the final report for AECB I.D. NO. H 1103472220 has been further developed to decrease interference from other elements, notably zirconium and halfnium (see Table 1 for a compilation of cross reactivities). Several changes are responsible for the decreased interference, in particular, very tight control of the pH of the sample and standards, increase in the concentration of the pH 1.5 wash solution and addition of arsenazo III to the 2 N HN03 after the back extraction step.

2. Analysis of Water, Aerosol and Solid Samples

The pH of the samples is particularly important for thorium extraction and uranium interference and should be kept between 1.45 and 1.55. For this reason, the between sample wash solution has been changed from 2 N HN03 to water so that resudual acid in the lines will not change the sample pH.

Standards are made up in 10% aluminum nitrate at pH 1.50 containing 0.5 mg/ml lanthanum and 0.1% HF to compensate for the dissolved lanthanum fluoride precipitate in the samples.

The autoanalyzer is set up as in the flow diagram, Figure 1 following general techniques for connecting components and tubing as outlined in the Technicon Users Manual. The system is "primed" for 10 minutes by pumping water through the lines which will carry aqueous reagents, and kerosene through the line which will be used for the thenoyltrifluoroacetone in kerosene reagent. The analyser is then switched over to pump reagents in all lines.

After a steady baseline has been maintained for at least 10 minutes, the samples and standards can be run. Aliquots of 2-3 ml of standards and samples are transferred into individual sample cups and placed in the sample tray. Typically, two calibrating standards of 1.0 ug/ml Th are run to set the full scale readout followed by a series of standards covering the 0.1 to 1.0 ug/ml Th range, then 2 blanks (standard diluent solution), then the samples, each separated by a blank, and finally a 1.0 ug/ml Th standard to check for changes in the calibration.

As the sample enters the autoanalyzer it is air segmented then mixed with 0.08 M thenoyltrifluoroacetone (TTA) in kerosene. The mixture passes into a 20 turn mixing coil where the extraction of the thorium (IV) into the organic phase takes place. At pH 1.5 thorium is strongly extracted into the organic phase while rare earths are only extracted at pH greater than 2. The mixture proceeds to a phase separator where the aqueous phase plus a small amount of the organic phase is pulled off to waste. The two phases are separated by virtue of their different densities. Clean separation is aided by a small teflon insert which "guides" the organic phase. The organic phase plus the segmenting bubble is then mixed with a "wash" solution of 20% saturated ammonium acetate pH adjusted to 1.5, and the phases separated with the wash solution going to waste. The pH 1.5 wash and separation step is then repeated. During the wash steps, any rare earths in the organic phase are back extracted into the wash solution. The organic phase is then mixed with 2 N HN03 in a 20 turn mixing coil to back extract the thorium into the aqueous phase and the organic phase separated to waste. Thorium is fully back extracted at pH less than 0, whereas other major interferring elements such as zirconium, hafnium and uranium are not. By adding arsenazo III after the back extraction step, formation of complexes between arsenazo III and interfering elements is avoided during the back extraction.

Arsenazo III color reagent (0.02% in water containing 1% Technicon Brij-35) is then added to the aqueous phase and mixed in a 5 turn mixing coil and the solution pumped into the colorimeter where the absorbance at 660 nm is measured. The time between the start of sample aspiration and the appearance of the peak on the chart recorder is approximately 8 minutes.

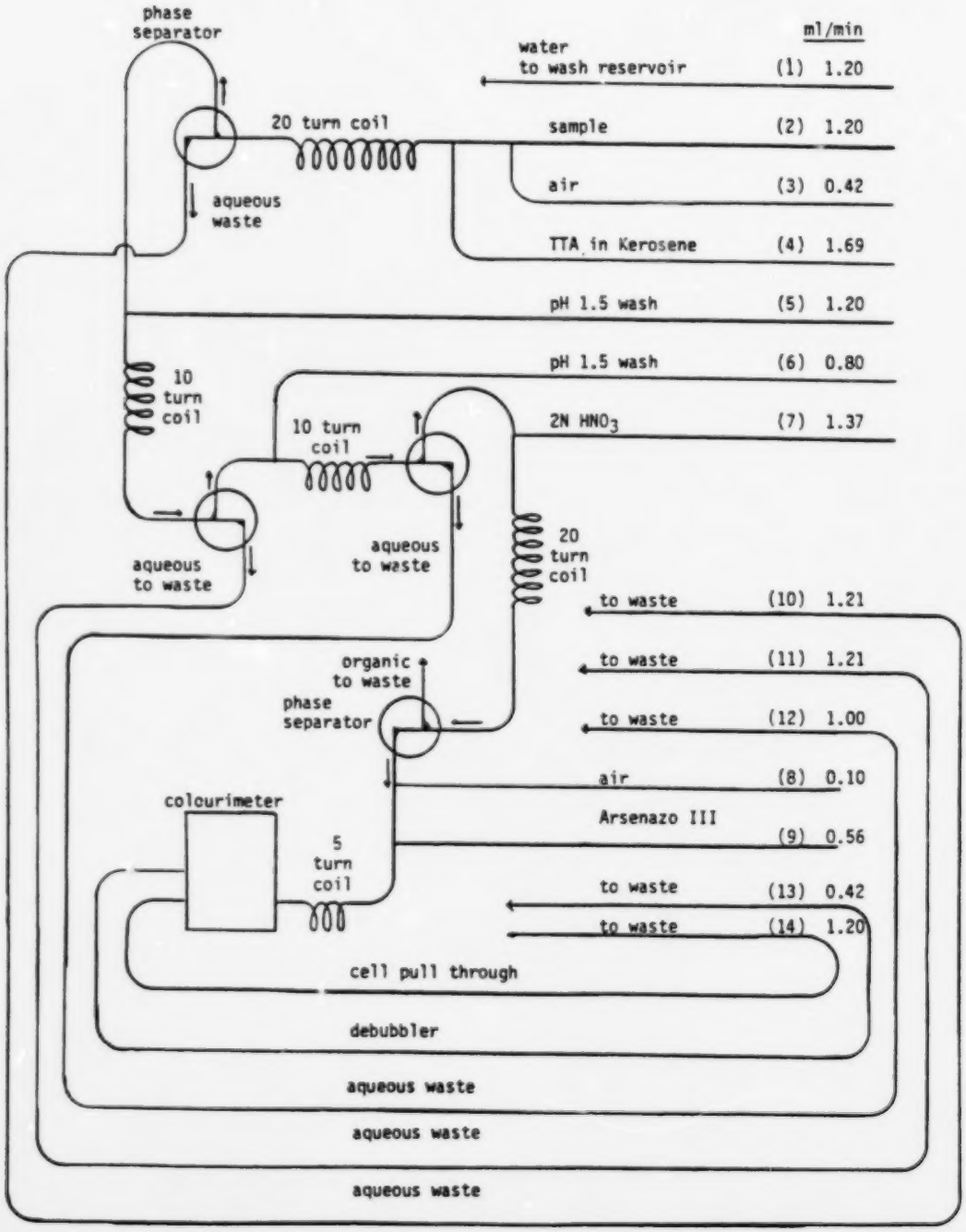
C. SAMPLE THROUGH-PUT

A batch of 12 water samples, taken from storage already filtered and acidified, may be processed up to the autoanalyzer stage in about three hours. Chemical yield determination would require approximately one hour further, depending upon the quantity of thorium-234 added and the counting equipment used for its assay. Processing of several standards and the 12 samples through the autoanalyzer would take about 1.5 hours, given that the machine is set up and ready to run. Data reduction and results documentation would require about one hour. Allowing about one hour for miscellaneous tasks, such as reagent preparation and machine set-up, leads to a total elapsed time of seven to eight hours for the processing of 12 water samples. The labour input would be about six person-hours, 0.5 person-hours per sample.

A batch of 12 solid or aerosol samples may be processed up to the autoanalyzer stage in about seven hours. Allowing one hour each for chemical yield determinations, autoanalyzer process, data reduction and miscellaneous tasks results in a total elapsed time of 11 hours. The total labour input would be about eight person-hours, or about 0.67 person-hours per sample.

FIGURE 1:

FLOW DIAGRAM FOR PROPOSED MODIFIED METHODOLOGY FOR THORIUM ANALYSIS ON TECHNICON AA II



REFERENCES

1. E.K. Hyde, The Radiochemistry of Thorium, National Academy of Sciences (U.S.A.) publication NAS-NS 3004 (1960). Available from National Technical Information Service, U.S. Department of Commerce, Springfield, Virginia 22161.

OTHER REFERENCES NOT QUOTED IN THE TEXT

2. Radiochemical Procedures for Determination of Selected Members of the Uranium and Thorium Series, CANMET Report 78-22, 1979, G.L. Smithson (Ed.).

3. R.H. Gaddy, Automated Procedures for Lithium, Cobalt and Thorium and Their Applications in Nuclear Process, Technicon Symposium, "Automation in Analytical Chemistry, "New York, September 9, 1965. (R.H. Gaddy, Savannah River Laboratory, E.I. du Pont de Nemours and Co., Aiken, S.C.).

4. J.R. Prall, The Automatic Determination of Thorium in Aqueous and Organic Solutions, Advances in Automated Analysis. (J.R. Prall, National Lead Company of Ohio, Box 39158, Cincinnati, Ohio 45239).

APPENDIX A

TABLE 1

CROSS REACTIVITY

ELEMENT	CONCENTRATION	CROSS REACTIVITY ORIGINAL METHOD	NEW METHOD
Zirconium	100 ppm	0.50%	0.01%
Cerium	100 ppm	0.10%	0.03%
Uranium	100 ppm	0.02%	0.01%
Hafnium	100 ppm	0.85%	0.10%

Cross reactivity is calculated as:

$$\frac{\%\ \text{response relative to 1 ug/ml Th}}{\text{concentration in ug/ml}}$$

TABLE 2

RESULTS OF ANALYSIS OF SOLID SAMPLES

SAMPLE	DESCRIPTION/ WEIGHT (g)	CHEMICAL YIELD %	Th CONTENT ug/g	Th MEASURED ug/g
1	SO-1 0.507	94	11.7	11.5
2	SO-1 0.440	86	11.7	11.4
3	SO-1 0.520	99	11.7	11.7
4	SO-1 0.533	87	11.7	12.9
5	SO-1 0.585	80	11.7	12.4
6	SO-1 0.475	96	11.7	11.0
7	SO-1 0.511	79	11.7	11.6
8	SO-2 0.462	81	3.7	2.4
9	SO-2 0.505	85	3.7	3.2
10	SO-2 0.517	83	3.7	3.5
11	SO-3 0.504	91	3.7	3.9
12	SO-3 0.482	88	3.7	3.0
13	SO-3 0.508	92	3.7	3.2
14	SO-4 0.524	77	8.2	7.0
15	SO-4 0.510	87	8.2	6.4
16	SO-4 0.510	77	8.2	5.1
17	Sarm3 0.385	93	65	67.6 *
18	Sarm3 0.520	96	65	58.0 *
19	UTS-4 0.506	92	15.4	13.1 +
20	STSD-2 0.522	88	16.0	16.0
21	STSD-3 0.420	75	8.3	8.7
22	LKSD-3 0.420	92	11.2	10.6
23	LKSD-1 0.484	86	2.1	2.0
24	Blank	31	0	< 1.0 **
25	Blank	33	0	< 1.0 **
26	Blank	90	0	< .5 **
27	Th spike	52	9.8	9.7
28	Th spike	22	6.3	6.7
29	1 mg Zr	90	0	< 0.5 **
30	0.5 mg Hf	92	0	0.6 **

* certified reference material (National Institute for Metalurgy, South Africa) Zr = 1.1%, Hf = 190 ug/g for this sample.
\+ certified value - CANMET
Note: other values are information values.

** assume 0.5g sample weight.

mean of 7 SO-1 samples 11.8 ug/g, SD = .6 (5%)

Blanks were processed in a manner identical to samples throughout the entire procedure.

TABLE 3

RESULTS OF ANALYSIS OF "AEROSOL SAMPLES"

SAMPLE	DESCRIPTION	CHEMICAL YIELD %	Th CONTENT ug	Th MEASURED ug
1	Membrane filter + 10.3 mg DH-1a*	99	9.6	8.4
2	Membrane filter + 5.2 mg DH-1a*	93	4.7	5.0
3	Teflon filter + 11.6 mg DH-1a*	81	10.8	10.2
4	Glass fibre filter + 11.1 mg DH-1a*	84	10.3	10.2

* Canmet certified reference material

TABLE 4

RESULTS OF ANALYSIS OF WATER SAMPLES

SAMPLE DESCRIPTION	CHEMICAL YIELD %	Th CONTENT ug/L	Th MEASURED ug/L
Mississauga tap water	70	?	< 1.0
Tap water + 2.0 ug/L Th	81	2.0	1.9
Tap water + 20 ug/L Th	81	20.0	21.0
AECB #1169	94	?	532
AECB #1169 + 1 ug/L Th	93	+1	538
AECB #1169 +20 ug/L Th	84	+20	571
AECB # 929 (not filtered)	85	?	19.8
AECB # 929 (filtered)	79	"	21.8
Ottawa Tapwater	86	?	0.4
Ottawa Tap + 10 ug/L	88	+10	11.4

APPENDIX B

STEPWISE PROCEDURES FOR SAMPLE PREPARATION

Water Samples

1. Transfer 500 ml of sample to a clean 1000 ml polymethylpentene (PMP) beaker.

2. Add 1 ml thorium-234 tracer solution.

3. Add 1 ml iron carrier solution.

4. Thoroughly stir the solution, then add 15 ml 7.5 N NH4OH solution while continuing to stir.

   See Steps 5(a) - 10(a) for alternative to steps 5 - 14.

5. Cover the beaker and wait at least 1 hour.

6. Set up the Millipore vacuum filter manifold and pump with 25 mm glass-fibre filters under glass-wool plugs and 50 ml extension barrels in place. The manifold reservoir should be empty and any filter ports not to be used should be closed with neoprene stoppers.

7. Filter the solutions, pausing to drain the filter manifold (volume approximately 2.5 L) as required. Discard the solutions to waste.

8. Wash each ferric hydroxide precipitate on the filter under slight vacuum with 3-5 ml water.

9. Switch off the pump, drain the manifold to waste and, keeping the two top plates of the manifold firmly together, remove them from the manifold and place on a clean surface.

10. Wipe out the interior of the manifold and insert the test tube holder with the appropriate number of 16 x 125 mm polycarbonate test tubes in place.

11. Re-assemble the manifold and connect to the pump but do not switch on the pump.

12. Add 10 ml 2 N HN03 to each precipitate and thoroughly stir using a disposable polyethylene pasteur pipet.

13. Apply slight vacuum to the filters to pull the solution through to the collecting tubes.

14. Switch off the pump and rinse the filters and glass wool plugs with a further 5 ml 2 N HN03, and apply vacuum to pull the wash through.

5(a). Cover the beaker and allow to stand overnight.

6(a). Decant to waste, as much of the clear supernatant as possible. Transfer the remaining supernatant and precipitate to 50 ml polycarbonate centrifuge tubes using as few tubes as possible for each sample.

7(a). Centrifuge for 5 minutes at 1500 rpm and decant the supernatant to waste from each tube.

8(a). Wash the precipitate in each tube with 10-20 ml of water mixing vigorously to resuspend the precipitate. Combine all of the precipitates for each sample into one tube. Centrifuge for 5 minutes at 1500 rpm.

9(a). Decant the clear supernatant to waste.

10(a). Add 15 ml 2 N HN03 to each tube and stir thoroughly to dissolve. Add additional 2 N HN03 1 ml at a time to entirely dissolve the precipitate. Continue procedure at step 15.

15. Add 1 ml lanthanum carrier solution (5 mg La) to each sample and mix thoroughly using a plastic stir-stick.

16. Add 3 ml 14 N HF and stir. Remove stir-stick.

17. Digest precipitate at least 1 hour in a 80 degree celsius water bath or overnight at room temperature.

18. Centrifuge tubes at 2000 rpm for 5 minutes and carefully decant supernatant to waste.

19. Wash precipitate with 10 ml water. Repeat the centrifuge step and decant supernatant to waste.

20. Add 5 ml 10% Al(N03)3 pH 1.5 to precipitate. Stir using a polyethylene pasteur pipet and place in a 80 degree celsius water bath for 15 minutes to effect dissolution of the precipitate.

21. Cool to room temperature and adjust to pH 1.50 $\pm$ .05 using .5 N HN03, or .5 N NH40H.

22. Transfer to 10 ml volumetric flasks and make up to 10 ml with 10% Al(N03)3 pH 1.5 solution.

23. Gamma-count the solutions in the volumetric flasks to determine chemical yield. Integrate the spectra between 60 and 95 keV. Subtract backgrounds similarly counted and integrated. Compare sample solution counts with 1 ml of tracer taken directly as a comparator and made up to 10 ml in a volumetric flask.

24. Transfer the solutions to plastic bottles pending the autoanalyzer finishing process.

Aerosol and Solid Samples

1. Place each aerosol sample and filter in a 100 ml polymethylpentene beaker, or weigh powdered ($\leq$ 100 mesh) solid samples (up to 0.5 g) into 100 ml polymethylpentene (PMP) beakers.

2. Add 1 ml thorium-234 tracer solution.

3. Add 5 ml each of 8 N HN03, 6 N HCl and 14 N HF.

4. Cover beakers with close fitting plastic watch-glasses (do not use Speedy-Vap ribbed cover) and place on hotplate with surface temperature about 125 degrees celsius for 2 hours.

5. Remove beaker covers but leave beakers on the hotplate. Add 25 ml 5% boric acid to each sample. Leave beakers uncovered on hot-plate for 1 hour further.

6. Set up Millipore vacuum filtration manifold with glass-fibre filter discs and 50 ml polycarbonate centrifuge tube receivers in place as appropriate . Place glass-wool plugs over the exposed filter surface for solid samples to hold back the precipitate to come. Close with neoprene stoppers any manifold ports which are not to be used. It is convenient to use the manifold extension barrels for solid samples for this filtration.

7. Pass the sample solutions through the filters and wash the PMP beakers and filters each with 5 ml water, rinsing any aerosol filter substrate residues into the filtration manifold. Note that each filtrate and wash combined should not exceed 40 ml.

8. Add 1 ml lanthanum carrier solution (5 mg La) to each centrifuge tube and mix thoroughly using a plastic stir-stick.

9. Add 3 ml 14 N HF and again stir. Remove the stir-stick.

10. Place tubes on water-bath at about 80 degrees celsius for at least 1 hour or leave overnight at room temperature.

11. Spin tubes at 2000 rpm for 5 minutes then decant supernatant solution to waste.

12. Wash precipitate with 10 ml of water. Repeat the centrifugation step and decant the wash solution to waste.

13. Add 5 ml 10% Al(NO3)3 pH 1.5 to precipitate. Stir using a polyethylene pasteur pipet and place in a 80 degree celsius water bath for 15 minutes to effect dissolution of the precipitate.

14. Adjust pH of cool solutions to 1.50 $\pm$ .05 with .5 N HNO3 or .5 N NH4OH.

15. Transfer solution to 10 ml volumetric flasks and make up to 10.0 ml with 10% Al(NO3)3 pH 1.5.

16. Gamma-count the solutions in the volumetric flasks to determine chemical yield. Integrate the spectra at 60 and 95 keV. Subtract backgrounds similarly counted and integrated. Compare sample solution counts with 1 ml tracer solution taken directly as a comparator and made up to 10 ml in a volumetric flask.

17. Store the solutions in plastic bottles pending the autoanalyzer finishing process.

APPENDIX C

STEPWISE PROCEDURES FOR TRACER PREPARATION

Anion-exchange Column Preparation

1. Dissolve 35 g U03 or U308 in 1.2 L 9 N HCl. Filter the solution through a glass wool plug to remove insoluble material. Store the solution in a narrow necked vessel.

2. Prepare approximately 250 ml anion exchange resin bed in 9 N HCl in 2.5 x 50 cm column. Resin: AGl-X8 100-200 mesh, Cl- form (Bio-Rad); Column: Econo-column 2.5 x 50 cm (Bio-Rad) plus funnel (Bio-Rad).

3. Place a glass-wool plug on top of the resin bed. Remove the funnel and install the column cap with luer fitting. Stop column flow with blank luer bottom fitting. Always leave a head of solution above the glass wool plug.

4. Attach thin tygon or equivalent plastic tubing to the cap luer fitting. Insert the free end of this tubing into the uranium solution container. Remove the bottom luer blank fitting and allow the column solution to flow into a narrow neck container of at least 1.5 L volume. The uranium solution will be syphoned through the column.

5. After the bulk of the uranium solution has passed through the column, remove the column cap with tube attached and wash out with water. Allow the uranium loading solution level to reach the resin surface, then wash the column walls above the resin surface with 2 x 10 ml 9 N HCl. Replace the blank luer bottom fitting to stop the flow and leave approximately 10 ml 9 N HCl head solution on the column.

6. When convenient, elute the column by syphon action (as above) with 1 L 9 N HCl to free the column from thorium. Leave column with approximately 10 ml 9 N HCl head solution and close both ends. The column is now ready for tracer production after a suitable period has elasped for build-up of thorium-234.

Note that the column eluents and effluents are radioactive and give off HCl fumes. They should be appropriately handled, preferably in a fume-hood.

Tracer Elution

1. Elute the column with 150 ml 9 N HCl, preferably by syphon action to avoid HCl fumes. Collect the eluate in a partially covered 600 ml glass beaker.

2. Evaporate the solution to approximately 10 ml volume in a fumehood and then add about an equal volume of 9 N HCl.

3. Pass the solution over a 0.7 x 5 cm column of AG1-X8 100-200 mesh, Cl- form resin conditioned in 9 N HCl. Collect effluent in 100 ml glass beaker.

4. Evaporate the column effluent solution to dryness. Dissolve the residue in 10 ml 8 N HN03 and pass over an identical column as in 3. above but conditioned in 8 N HN03. Then wash the column with 2 x 5 ml 8 N HN03.

5. Elute the thorium tracer with 20 ml 1 N HCl and dilute with water to the desired volume. Store in a screw cap polyethylene bottle.

The yield of this process is about 70% of the thorium present on the generator column.

APPENDIX D

STEPWISE PROCEDURE FOR AUTOANALYZER PROCESS - ALL SAMPLES

1. Using the flow diagram Figure 1, Section B as reference, check that all tubing and components on the autoanalyzer are in place.

2. Prepare reagents as required from the flow diagram. Prepare 0.1, 0.2, 0.5 and 1.0 ug/ml Th standards in standard diluent solution. Check that all standards and samples are at pH 1.50 $\pm$ .05, adjust if necessary.

3. Prime the system for 20 minutes by pumping water through all reagent and sample lines except line for TTA in kerosene. Pump kerosene through this line. Check bubble pattern, phase mixing in coils and phase separation at phase separators. Minor changes will be seen when system is switched to reagents. Check that there are no leaks. Turn on colorimeter.

4. Switch lines over to reagents. The amounts indicated in Appendix E should be sufficient for a typical 2 hour run. Pump for 15 minutes.

5. Check bubble pattern, phase mixing in coils and phase separation. The air bubbles should be evenly spaced and effectively sweeping the reagents through the system. There should be good interaction of the organic and aqueous phases in the mixing coils to optimize extraction. In the first, second and third phase separators, there should be no aqueous solution in the diverted organic phase and only a small loss of organic phase to the aqueous phase. At the final phase separation, there must be no organic phase going into the aqueous fraction. Check that there are no air bubbles in the cell pull through line.

6. Turn on recorder and adjust optics to achieve baseline at zero deflection on chart recorder (see Technicon Manual).

7. Place 2-3 ml each of standard and sample solutions in sample tray as follows: duplicate calibration standards of 1.0 ug/ml thorium, duplicates of each diluted standard, 2 blank solutions, samples alternating with blank solutions, and a final 1.0 ug/ml standard. Use standard diluent solution for blanks.

8. After baseline has been steady for 10 minutes, start run. First peak will appear in 6-8 minutes. Adjust standard calibration potentiometer so that the response is 100% full scale for the first two calibration standards. Check that good hydraulics are maintained throughout run.

9. Turn off sampler after the last sample and standards have been aspirated.

10. After last peak has appeared, wash out analyzer for at least 10 minutes with water in all reagent lines except Arsenazo III line. Wash out Arsenazo III line with 10% NaOH for 5 minutes, followed by water for 5 minutes.

11. Prepare a calibration curve by plotting percent chart deflection vs ug/ml of thorium in standards. Amount of thorium in the original sample in micrograms is ten times the concentration found in ug/ml corrected for chemical yield using thorium tracer.

APPENDIX E

PREPARATION OF REAGENT SOLUTIONS

1. Hyrochloric Acid 9 N

   Dilute 1.5 L reagent grade concentrated hydrochloric acid to 2 L with water.

2. Iron carrier, 5 mg/ml Fe

   Dissolve 4.3 g $FeNH_4(SO_4)_2.12H_2O$ in 100 ml deionized water.

3. Ammonium hydroxide 7.5 N

   Dilute reagent grade concentrated ammonium hydroxide solution 1:1 with water.

4. Nitric acid 2 N

   Dilute 100 ml reagent grade concentrated nitric acid to 800 ml with water.

5. Lanthanum carrier, 5 mg/ml La

   Dissolve 1.6 g $La(NO_3)_3.6H_2O$ in 100 ml deionized water.

6. Hydrofluoric acid 14N

   Dilute reagent grade concentrated hydrofluoric acid 1:1 with water.

7. Aluminum nitrate 10%, pH 1.5

   Dissolve reagent grade $Al(NO_3)_3.9H_2O$ in water, e.g. 100 g in 1 L. Adjust to pH 1.50 $\pm$ .05 using dilute nitric acid and/or ammonium bydroxide.

8. Nitric acid .5 N

   Dilute 10 ml reagent grade concentrated nitric acid to 320 ml with water.

9. Ammonium Hydroxide .5 N

   Dilute 10 ml reagent grade concentrated ammonium hydroxide to 300 ml with water.

10. Hydrochloric acid 6 N

Dilute reagent grade concentrated hydrochloric acid 1:1 with water.

11. Nitric acid 8 N

Dilute reagent grade concentrated nitric acid 1:1 with water.

12. Boric acid 5%

Dissolve reagent grade boric acid in water, e.g. 50 g in 1 L.

13. Thenoyltrifluoroacetone (TTA) 0.08 M

Dissolve 5.3 g TTA in 300 ml kerosene. (May require slight warming to completely dissolve.) This amount is sufficient for a 2 hour run.

14. Ammonium acetate wash solution, pH 1.5

Prepare a saturated stock solution of ammonium acetate in water. Dilute 200 ml of this to 800 ml with water and adjust to pH 1.48 to 1.52 with 2N nitric acid and dilute ammonium hydroxide and make up to 1 L.

15. Arsenazo-III 0.02% in water

Dissolve 0.020 g Arsenazo-III in 100 ml deionized water. Add 1 ml Technicon Brij 30% solution. Filter the solution through a Whatman #40 filter paper. This amount is sufficient for a 2 hour run. Make up fresh for each run.

16. Standard Diluent Solution

Dissolve 50 g Al(N03)3.9H20, and 0.77 g La(N03)3.6H20 in 400 ml water. Add 1.0 ml 14 N HF and adjust to pH 1.48 - 1.52. Make up to 500 ml with water.

17. Thorium standards

Dilute 1000 ppm thorium atomic absorption standard solution with standard diluent solution (sol 16) to appropriate concentrations in the range 0.0-1.0 ug/ml thorium.

USE ONLY ANALYTICAL REAGENT GRADE CHEMICALS